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ON THE FREE ENERGY OF A MIXTURE OF IONS: AN EXTENSION OF KRAMERS' THEORY*

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ABSTRACT

A theory of electrolytes founded on the principles of statistical mechanics is presented. The primary physical assumptions are: 1) point ions; and 2) small fluctuations. The theory is a modification of Kramers' theory of electrolytes. The modification consists of a more physically accurate development of assumption 2). The main result of the present theory is that a partition function for the electrolyte is obtained for all concentrations whereas Kramers' theory breaks down beyond a limiting concentration. The deviation from the Debye-Hueckel limiting law is in the direction of the experimental observations.

INTRODUCTION

In the early days of the development of the theory of strong electrolytes, Kramers[1] showed that the Debye-Hueckel low concentration limiting laws could be derived from the statistical mechanical partition function as well as from the Poisson-Boltzmann differential equation. However, with increasing concentration the Kramers and experimental results diverged in opposite directions from the Debye-Hueckel limiting laws. This can be seen in Fig. 1 where the osmotic coefficient[2] is plotted[3] as a function of the square root of the concentration for a (1-1) salt, a salt of NaCl type.

An especially interesting feature of Kramers' theory is the existence of a critical concentration above which the partition function becomes a complex number. To understand Kramers' interpretation of this result let us suppose

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[1] H.A. Kramers, Proc. Roy. Acad. Amsterdam XXX, 145 (1927).

[2] The osmotic coefficient was defined by N. Bjerrum as follows. Let $\overline{P} = NkT$ be the osmotic pressure of a solution of N independent (non-interacting) ions. Also, let $P = gNkT$ be the osmotic pressure of the corresponding real solution in which the ions interact with each other. Here g is the correction factor to $\overline{P}$ for a real solution. The ratio $(\overline{P} - P)/\overline{P} = 1 - g$ is the osmotic coefficient.

[3] Detailed accounts of the observed behavior of electrolytes and of the consequences of the Debye-Hueckel theory are given in the two treatises: a) H. Falkenhagen, Electrolytes, Oxford (1934); b) Harned and Owens, The Physical Chemistry of Electrolytic Solutions, Reinhold (1950). Very few references to the classical papers will be given here. They can be found in a) and b).

that we have obtained an exact formula for the osmotic coefficient of a system of ions of ionic radius a. A curve such as one of those plotted in Fig. I could be drawn for each value of a. In particular there would be a limit curve as a → 0. If the result of Kramers were exact, the critical concentration would be that concentration above which the limit curve would not exist. Physically this might mean that if the concentration of a dilute solution of point ions were gradually increased, a sudden association of oppositely charged ions would occur at the critical concentration with a correspondingly sudden drop in the osmotic coefficient.

The Kramers critical concentration is quite low, and corresponds to 0.03 mol per liter for KCl in water at 15°C and to 0.0005 mol per liter for $MgSO_4$. Even though real ions have non-vanishing ionic radii, one would expect that if the association divergence in the osmotic coefficient for point ions were correct, then some residue of it should still appear in the experimental curves in the neighborhood of the critical concentration. Actually the experimental deviations from the limiting laws for some "small ion" salts (KNO_3) do not become significant until the concentration is considerably higher than the critical one.

Since Kramers' paper contains several mathematical approximations, to which he called attention, we have felt that it would be of interest to see whether or not his qualitative results depend on the mathematical approximations. By replacing what we consider to be Kramers' most severe approximation by one that is physically more reasonable, we shall show that the divergence at the critical concentration disappears and that the new deviations from

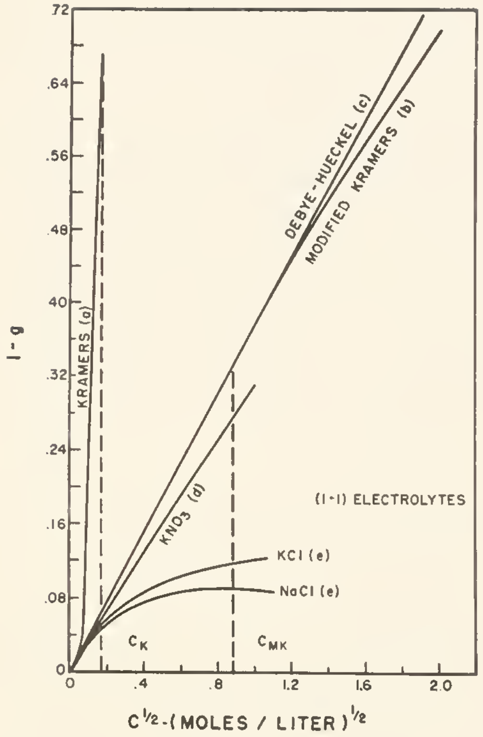

Fig. 1. The osmotic coefficient, $1 - g$, as a function of the square root of the concentration, C for a (1-1) electrolyte. a) The Kramers' Theory: $C_K = .029$ moles/liter. b) The Modified Kramers' Theory: $C_{MK} = .78$ moles/liter. c) The Debye-Hueckel Limiting Law. d) Scatchard and Prentiss J. Am. Chem. Soc., 44, 2690 (1932). e) Scatchard and Prentiss, J. Am. Chem. Soc., 55, 4355 (1933).

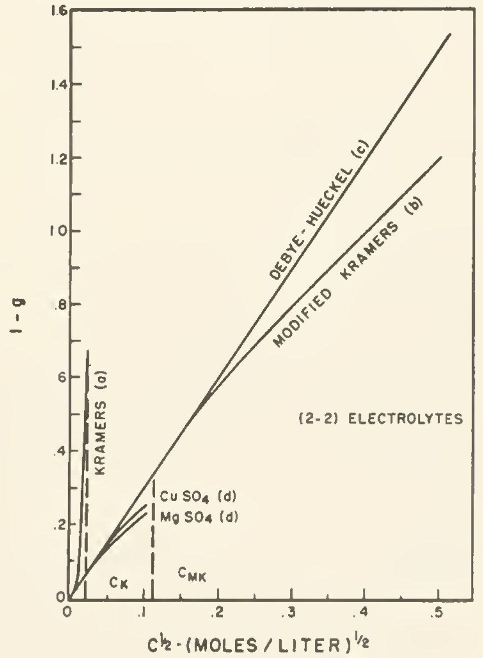

Fig. 2. The osmotic coefficient, $1 - g$, as a function of the square root of the concentration, C, for a (2-2) electrolyte. a) The Kramers' Theory: $C_K = .00048$ moles/liter. b) The Modified Kramers' Theory: $C_{MK} = .013$ moles/liter. c) The Debye Hueckel Limiting Law. d) Hovorka and Rodebush, J. Am. Chem. Soc., 49, 647 (1927).

the Debye-Hueckel limiting laws (for point ions) are in the same direction as the experimental deviations. Inasmuch as we do not include short range repulsive force parameters in the theory, we obtain a single function for thermodynamic quantities of salts of a given ionic type rather than the family of functions that has been observed experimentally.

KRAMERS' THEORY OF ELECTROLYTES

We shall present the main features of Kramers' theory. ~~This~~ is done because Kramers' really elegant analysis is not widely known and because our modification will then be readily understandable.

Let N ions with charges $\epsilon_1, \epsilon_2, ---, \epsilon_N$ be located at positions $\vec{r}_1, \ldots, \vec{r}_N$ in a container of volume V. The thermodynamic properties of this system can be computed from the partition function

$$Z = V^N \exp[-\Delta\psi/kT] = \int_V \cdots \int d\tau_1 \cdots d\tau_N \exp[-U(\vec{r}_1, \cdots, \vec{r}_N)/kT] \tag{1}$$

Here $d\tau_j$ is the volume element of the jth ion and $U(\vec{r}_1, \ldots, \vec{r}_N)$ is the total potential energy of interaction of all the ions. The symbol $\Delta\psi$ denotes the deviation of the free energy of the system of ions from that of a system of N independent point particles.

It was discovered by early workers that if $U(\vec{r}_1, \ldots, \vec{r}_N)$ represents only Coulomb interactions,

$$U(\vec{r}_1, \cdots, \vec{r}_N) = D^{-1} \sum_{j<k} \epsilon_j \epsilon_k / r_{jk} \quad , \tag{2}$$

(D = dielectric constant of the solvent and r_{jk} is the distance between the jth and kth ions), then the thermodynamic quantities computed on the basis of (1) diverge. This short range divergence does not really occur because of the existence of short range repulsive forces. In the work of Kramers the divergence is avoided by essentially excluding ionic configurations involving very short distances.

Kramers' analysis is based on a theorem of O. Klein[4] which states that if $U(\vec{r}_1, \ldots, \vec{r}_N)$ is a homogeneous function of degree μ, that is, $U(\lambda\vec{r}_1, \ldots, \lambda\vec{r}_N) = \lambda^{\mu} U(\vec{r}_1 \ldots, \vec{r}_N)$, then, for N sufficiently large,

$$\exp[-\Delta\psi/kT] = [F(n^{-\mu/3}/kT)]^N$$

where n is the number of particles per unit volume and F is some function of $(n^{-\mu/3}/kT)$. Klein's Theorem can not be applied if the ionic radius or any of the usual expressions for the repulsive forces is introduced because the homogeneous character of the potential energy function is lost.

The Coulomb interaction as a function of distance is an homogeneous function of degree -1. In order to avoid the short range divergence and preserve the homogeneity of (2), Kramers replaces (2) by

$$U(\vec{r}_1, \ldots, \vec{r}_N) = D^{-1} \sum_{j<k} \epsilon_j \epsilon_k g_{jk} , \qquad (3)$$

where

$$g_{jk} = r_{jk}^{-1} [1 - \exp(-\lambda h_{jk})] ,$$

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[4] O. Klein, Medd. K. Vet. Nobelinstitute, 5, No. 6, (1919).

$$h_{jk}^2 = r_{jk}^2/4R_{jk}^2 = \frac{(x_j - x_k)^2 + (y_j - y_k)^2 + (z_j - z_k)^2}{(x_j + x_k)^2 + (y_j + y_k)^2 + (z_j + z_k)^2} .$$

As $r_{jk} \rightarrow 0$, $g_{jk} \rightarrow 0$. However, if λ is chosen to be a very large number, then $g_{jk} = r_{jk}^{-1}$ except when r_{jk} is extremely small. By locating the origin of the coordinate system outside the volume V, R_{jk} is of order $V^{1/3}$. Since the mean distance between ions is of order $n^{-1/3}$, $n = N/V$, h_{jk} is of order $N^{-1/3}$. Hence, by choosing λ to be of order $N^{2/3}$ the potential energy function (3) does not differ significantly from the Coulomb function even for r_{jk} considerably smaller than the mean distance between ions. When there is considerable association of oppositely charged ions, i.e. at high concentrations, (3) cannot be expected to give quantitative results. Since the constant λ does not appear in the final results, there is no way of varying the thermodynamic properties with the characteristics of the repulsive forces.

In his detailed calculations, Kramers does not use (1) but a partition function analogous to the Gibbs grand partition function. His generalized ensemble is such that for a given configuration of the centers of the N ions, the charge on a given ion may assume any value which the charge of an arbitrary ion can have. The new partition function is defined by

$$V^N \exp[-\Delta\psi/kT] = \int_V \cdots \int d\tau_1 \cdots d\tau_N \, N^{-N} \sum \exp[-U/kT] , \tag{4}$$

where the summation under the integral extends over all possible arrangements of the charges $\epsilon_1, \epsilon_2, \cdots, \epsilon_N$ on the ions located in the volume elements $d\tau_1, d\tau_2, \cdots, d\tau_N$.[5]

The total potential energy is a quadratic form in the charges $\{\epsilon_j\}$. Kramers diagonalizes this quadratic form by introducing a set of variables $\{y_j\}$ which are linear combinations of the variables $\{\epsilon_j\}$, $y_k = \sum_j \gamma_{kj} \epsilon_j$, and choosing the matrix (γ_{kj}) so that $U = \frac{1}{2} \sum_j b_j y_j^2$. The b's are the characteristic values of the matrix $(D^{-1} g_{kj})$.

In order to take advantage of the diagonalization, Kramers then assumed that the variables $\{y_j\}$ could be regarded as continuous variables and that the distribution of the set $\{y_j\}$ was Gaussian in each variable. The probability that y_k lay in the range dy_k was given by

$$(2\pi\eta)^{-1/2} \exp[-y_k^2/2\eta]\, dy_k \, .$$

Here η is a number proportional to the ionic strength and is the standard deviation from neutrality of a charge chosen at random in a solution.

It was noted by Kramers that the characteristic values $\{b_j\}$, which depend on the ionic configuration, are not all positive for every configuration. This implies that for T sufficiently small integration over y_k, say, would lead to an infinite value. It is the non-positive definite quadratic form coupled with

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[5] An investigation of thermodynamic fluctuations in this generalized ensemble has been made by S. Levine, Proc. Roy. Soc. A152, 529 (1935).

the assumption of statistically independent y_k's with Gaussian distribution which is responsible for the breakdown of Kramers' theory above a critical concentration. Increasing concentration is equivalent to decreasing temperature because, from Klein's Theorem, these two variables are equivalent to the single variable $n^{1/3}/T$.

This concludes our resume of Kramers' work. Further details involve the evaluation of the partition function (4), and these details will appear below in the evaluation of our modified partition function.

THE MODIFIED KRAMERS' THEORY

An important parameter of a system of ions is the reciprocal length κ which is defined by

$$\kappa^2 \equiv (4\pi/DkT) \sum_{i=1}^{s} (N_i/V)\, e^2 z_i^2 \quad , \tag{5}$$

where s is the number of ionic species, N_i is the number of ions of the ith species and ez_i is the charge on an ion of the ith species (e being the electron charge).

Let

$$\eta \equiv DkTV\kappa^2/4\pi N \quad . \tag{6}$$

This is a constant proportional to the ionic strength, and we may write, using equations (5) and (6),

$$\sum_{j=1}^{N} \epsilon_j^2 = N\eta \quad . \tag{7}$$

Our modification of Kramers' theory consists of computing thermodynamic averages over the ensemble restricted by Equation (7) for fixed η. A charge configuration in our ensemble will consist of a set of N ions with the properties:

a) $-(N\eta)^{1/2} \leqslant \epsilon_j \leqslant (N\eta)^{1/2}$ for all j;

b) $\sum_{j=1}^{N} \epsilon_j^2 = N\eta$;

the value of the sum in the real physical system of interest. Our complete ensemble will be the set of all systems of N ions with the proper ionic strength (i.e. with the proper value of $N\eta$) which are confined to a container of fixed shape and volume V at constant temperature T.

The average value of a function of position and charge, $F(\{\vec{r}_j\},\{\epsilon_j\})$, will then be

$$\langle F\rangle = Z^{-1}\underbrace{\int\cdots\int}_{\sum_{j=1}^{N}\epsilon_j^2=N\eta}\ \underbrace{\int\cdots\int}_{V} d\epsilon_1\cdots d\epsilon_N\, d\tau_1\cdots d\tau_N\, F(\{\vec{r}_j\},\{\epsilon_j\})\exp[-U/kT], \tag{8}$$

where Z is the partition function given by

$$Z = V^N \exp[-\Delta\psi/kT] = A\underbrace{\int\cdots\int}_{\sum_{j=1}^{N}\epsilon_j^2=N\eta}\ \underbrace{\int\cdots\int}_{V} d\epsilon_1\cdots d\epsilon_N\, d\tau_1\cdots d\tau_N \exp[-U/kT]. \tag{9}$$

The constant A is chosen so that as $T \to \infty$, $\Delta\psi \to 0$. A is the reciprocal of the surface area of an N-dimensional sphere of radius $(N\eta)^{\frac{1}{2}}$.

$$A^{-1} = 2\pi^{N/2}(N\eta)^{(N-1)/2}/\Gamma(N/2) \quad . \tag{10}$$

Before attempting to compute the above partition function let us compare the modified ensemble with that of Kramers. Kramers' basic partition function, Eq. (4), may be considered to be correct (to within the limitations inherent in the manner in which the Coulomb divergence is avoided as $r_{jk} \to 0$) at least for symmetrical electrolytes.* However, after making his mathematical approximations, Kramers' ensemble becomes one in which the $\{\epsilon_j\}$ are not limited to discrete values $ez_1, \ldots, ez_s$ but are allowed to range between $-\infty$ and $+\infty$ with the probability for ϵ_j to lie between ϵ_j and $\epsilon_j + d\epsilon_j$ given by $(2\pi\eta)^{-1/2} \exp[-\epsilon_j^2/2\eta]\, d\epsilon_j$. Averages are taken over all ϵ_k's and all $\vec{r}_k$'s. Since the $\{\epsilon_j\}$ are independent variables, the ionic strength for the systems in this ensemble ranges from 0 to ∞. The modified ensemble is that part of Kramers' ensemble which contains systems of the correct ionic strength. The ϵ_j's are not independent but connected through the relation $\sum_{j=1}^{N} \epsilon_j^2 = N\eta$. It is this property which makes the modified ensemble more representative of a real electrolyte than Kramers' ensemble.

To evaluate the partition function, Eq. (9), we (as did Kramers) take advantage of the fact that U is a quadratic form in the charges. Multiplying the integrand of Eq. (9) by the normalized delta function

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*See Ref. 5. Apparently in unsymmetrical salts some corrections might have to be made in the free energies.

$$\delta(\epsilon_1, \cdots, \epsilon_N) = \frac{2(N\eta)^{1/2}}{2\pi} \int_{-\infty}^{\infty} dx \exp\left[ix\left(\sum_{j=1}^{N} \epsilon_j^2 - N\eta\right)\right] , \tag{11}$$

we have

$$Z = A \int_{-\infty}^{\infty} \cdots \int \int_{V} \cdots \int d\epsilon_1 \cdots d\epsilon_N d\tau_1 \cdots d\tau_N \, \delta(\epsilon_1, \cdots, \epsilon_N) \exp\left[-U/kT\right] . \tag{12}$$

Rearranging the order of integration, we write

$$Z = A \pi^{-1} (N\eta)^{1/2} \int_{ix_0-\infty}^{ix_0+\infty} dx \exp[-ixN\eta] \int_{V} \cdots \int d\tau_1 \cdots d\tau_N \int_{-\infty}^{\infty} \cdots \int d\epsilon_1 \cdots d\epsilon_N \exp\left[ix \sum_{j=1}^{N} \epsilon_j^2 - (DkT)^{-1} \sum_{j<k} \epsilon_j \epsilon_k g_{jk} \right. \tag{13}$$

where the line ix_0 = constant, x_0 real and positive, is above the singularities of the integrand. The rearrangement is possible because U as defined in (3) is finite for all positional configurations of the ions. Therefore an x-domain will exist for which the quadratic form in the $\{\epsilon_j\}$ is negative definite. Thus, the integration over the $\{\epsilon_j\}$ will be finite. We then have that

$$\int_{-\infty}^{\infty} \cdots \int d\epsilon_1 \cdots d\epsilon_N \exp\left[ix \sum_{j=1}^{N} \epsilon_j^2 - (DkT)^{-1} \sum_{j<k} g_{jk} \epsilon_j \epsilon_k\right] = \pi^{N/2} / D_N^{1/2} , \tag{14}$$

where D_N is the determinant of the quadratic form in the exponent.

$$D_N \equiv \left| -ix\delta_{jk} + (2DkT)^{-1} g_{jk} \right| \quad ; \quad g_{jj} = 0 . \tag{15}$$

Therefore

$$Z = A(N\eta)^{1/2}\pi^{\frac{1}{2}N-1}\int_{ix_0-\infty}^{ix_0+\infty} dx\, \exp[-ixN\eta] \int_V \cdots \int D_N^{-1/2}\, d\tau_1 \cdots d\tau_N \,. \qquad (16)$$

We shall briefly digress in order to point out that the condition of electrical neutrality holds in the mean as it does in Kramers' theory. The total charge of a system is $Q = \sum_{j=1}^{N} \epsilon_j$ so that $\langle Q \rangle = N\langle \epsilon_j \rangle$. Now a linear, orthogonal transformation from the variables $\{\epsilon_j\}$ to variables $\{y_j\}$ exists such that the quadratic form in the $\{\epsilon_j\}$ becomes $\sum_j b_j y_j^2$. This means that $\langle \epsilon_j \rangle = \sum_{k=1}^{N} \gamma_{jk} \langle y_k \rangle$, the γ_{jk}'s being the transformation coefficients. Since the integrand in Eq. (13) becomes an even function of y_j for all j, then $\langle y_j \rangle = 0$ for all j and $\langle Q \rangle = 0$.

Now we may write

$$\exp[-\Delta\psi/kT] = A(N\eta)^{1/2}\pi^{\frac{1}{2}N-1}\int_{ix_0-\infty}^{ix_0+\infty} dx\, \exp[-ixN\eta]\, G_N \,, \qquad (17)$$

with

$$G_N \equiv V^{-N}\int_V \cdots \int D_N^{-1/2}\, d\tau_1 \cdots d\tau_N \equiv \langle D_N^{-1/2} \rangle_V \,. \qquad (18)$$

Following Kramers, if $\Delta\psi$ is to have thermodynamic sense, G_N would be the most probable value of $D_N^{-\frac{1}{2}}$ as $N \to \infty$, where x would be considered as

a parameter of external constraint on the system. Assuming that fluctuations are small, which is valid for not too high concentrations, Eq. (18) can be written as

$$G_N = \langle D_N \rangle_V^{-\frac{1}{2}} \tag{19}$$

This means that as $N \rightarrow \infty$, G_N is the reciprocal square root of the most probable value of D_N.

If we followed Kramers in applying Klein's Theorem to Eq. (18), we would have $G_N = \left[\phi(x, n^{1/3}/T)\right]^N$ for N sufficiently large, where ϕ is some function of the variables x and $n^{1/3}/T$. This approximation is not sufficiently exact for our purposes because the essential singularity of G_N is not properly characterized by the function ϕ. The essential singularity of G_N can be put in evidence by noting that the transformation from the variables $\{\epsilon_j\}$ to the variables $\{y_j\}$ is such that $\sum_{j<k} g_{jk}\epsilon_j\epsilon_k = \sum_{j=1}^{N} b_j y_j^2$.

We can then write

$$D_N = \prod_{j=1}^{N} \left[-ix + (2DkT)^{-1} b_j\right] \tag{20}$$

It is plain that we may write

$$\langle D_N \rangle_V = \prod_{j=1}^{N} \left[-ix + (2DkT)^{-1} \lambda_j\right], \tag{21}$$

where $(2DkT)^{-1}\lambda_j$ is one of the N roots of the polynomial $\langle D_N \rangle_V$. Since the matrix (g_{jk}) is real and symmetric, the roots are real and $|\lambda_j| \leq \lambda_m(N)$ where $\lambda_m(N)$ is the magnitude of the maximum root of $\langle D_N \rangle_V$. The maximum root may be independent of N. This also means that in Eq. (17) we must take

$x_o > (2DkT)^{-1}\lambda_m(N)$.

Let us put $\alpha^{-1} = -ix2DkT$, and write

$$\langle D_N\rangle_V = (-ix)^N \exp\left[N g_N\right] , \tag{22}$$

where

$$g_N(\alpha) = \frac{1}{N}\sum_{j=1}^{N} \ln(1+\alpha\lambda_j) .$$

The function $g_N(\alpha)$ is analytic in the region $|\alpha| < 1/\lambda_m(N)$.

Thermodynamic arguments require the existence of $g_N(\alpha)$ as $N \to \infty$, that is, $g_\infty(\alpha)$ must exist. Since $\lambda_m(N)$ exists for every N and since the radius of convergence is $1/\lambda_m(N)$ for every N, the existence of the limit function $g_\infty(\alpha)$ implies a non-zero radius of convergence and the consequence that $\lambda_m(N) \to \lambda_m(\infty) \equiv \lambda_m$, where a finite λ_m must exist. Therefore, λ_m may be determined from the radius of convergence of $g_\infty(\alpha)$ if this function can be found.

The existence of a finite λ_m has the following consequence. Since $|\lambda_j| \leq \lambda_m(N)$ for all j, the N roots are confined to a finite real interval. In general, the N roots will be all different. Therefore, as $N \to \infty$, the roots will become dense in the limit. It then follows that the behavior of $g_\infty(\alpha)$ as $\alpha \to 1/\lambda_m$, that is, the character of the singularity of g_∞ on the radius of convergence, depends on the limiting density of the λ_j. It is then clear that the character of the singularity of g_∞ has little to do with the single term $\ln\left[1 \pm \alpha\lambda_m(N)\right]$ in the sum g_N which exactly describes the singularity at $\alpha = \mp 1/\lambda_m(N)$ for every N. This means that an accurate description of $N g_N$ as $N \to \infty$ requires us to write

$$Ng_N \to \ln(1-\alpha\lambda_m) + Ng \quad , \quad |\alpha| < 1/\lambda_m \;, \tag{23}$$

where

$$g(\alpha) = \lim_{N\to\infty} \frac{1}{N} \sum_{\substack{j=1 \\ \lambda_j \neq -\lambda_m}}^{N} \ln(1+\alpha\lambda_j) \quad ,$$

and we have supposed that the singularity occurs at $\alpha = +1/\lambda_m$. Because the roots become dense in the limit, $g(\alpha) = g_\infty(\alpha)$. Hence, we are required to write

$$\langle D_N \rangle_V = (1-\alpha\lambda_m)(-ix)^N \exp[Ng] \tag{24}$$

as $N \to \infty$. It should be noted that the previously mentioned $\phi = \exp g$. This more accurate limiting expression for $\langle D_N \rangle_V$ does not influence the result obtained by Kramers.

The application of Klein's Theorem implies that g will be a function of the two variables x and $n^{1/3}/T$, or α and $n^{1/3}$, and that λ_m will be proportional to $n^{1/3}$.

Eq. (24) is equivalent to stating that for N large, $\langle D_N \rangle_V = O(M^N)$ where M is a function independent of N. We followed Kramers' thermodynamic reasoning to obtain this result. It is implicit in Klein's Theorem that the Nth root of the partition function integral be bounded as $N \to \infty$. It is clear, however, that the asymptotic behavior of D_N, and that of $\langle D_N \rangle_V$, depends on the properties of the elements of the determinant. For example, if $D_N = \det a_{ij}$ and if all that was known about the elements a_{ij} was that $|a_{ij}| \leqslant M$ for all i, j with M a positive constant, then the most one could state is the result of Hada-

mard's Theorem,[6] $|D_N| \leqslant N^{\frac{1}{2}N} M^N$. This implies that $|D_N|^{1/N} \leqslant MN^{\frac{1}{2}} \rightarrow \infty$ as $N \rightarrow \infty$. Thus, we would have no guarantee that a thermodynamic free energy per particle would exist independent of N, and Klein's Theorem could not be applied.

A condition on the elements a_{ij} sufficient to insure the existence of the required limit is easily found. The antecedent of Hadamard's inequality is that of Kelvin, Muir, and Hadamard[7] which states that

$$|D_N|^2 \leqslant \prod_{j=1}^{N} \left(\sum_{k=1}^{N} |a_{jk}|^2 \right) . \tag{25}$$

Hence if $\sum_{k=1}^{N} |a_{jk}|^2 \leqslant M^2$ for all j, then $|D_N| \leqslant M^N$ so that $D_N = O(M^N)$ if M exists. In our case,

$$\lim_{N\rightarrow\infty} \sum_{k=1}^{N} |a_{jk}|^2 = \chi^2 + \lim_{N\rightarrow\infty} \sum_{\substack{k=1 \\ k \neq j}}^{N} (2DkT)^{-2} g_{jk}^2 \tag{26}$$

$$\simeq \chi^2 + (2DkT)^{-2} \int_0^\infty f(r)\, r^{-2} \left[1 - \exp\{-\lambda h(r)\}\right]^2 dr ,$$

where f(r) is the radial distribution function of ions about a given ion. This is

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[6] Cf. Whittaker and Watson, Modern Analysis, Cambridge University Press, Fourth Edition, 1940, p. 212.

[7] Hardy, Littlewood, and Polya, Inequalities, Cambridge University Press, 1934 p. 34

an average value of the required sum. As $r \to \infty$, $h(r) \sim r/V^{1/3}$ and $f(r) \sim r^2$. Thus, the integral does not converge as N, $V \to \infty$, N/V finite. However, we can make the integral converge by introducing a summability factor $\exp\left[-\mu h(r)\right]$, μ a small, real, positive constant, into the force law, Eq. (3). Then

$$g_{jk} = r_{jk}^{-1}\left[1 - \exp(-\lambda h_{jk})\right] \exp(-\mu h_{jk}) \quad . \tag{27}$$

Once it is assumed through this factor that $\sum_k |a_{ik}|^2$ is bounded, then $D_N = O(M^N)$ and we are justified in employing Eq. (24) for $\langle D_N \rangle_V$.

Returning to Eq. (19) for G_N, we now have the result that the singularity of G_N is a branch point of order 1, and in the limit $N \to \infty$ occurs at $x = i(2DkT)^{-1}\lambda_m$.

We follow Kramers' method for determining the limiting function $g(x, n^{1/3}/T)$. Let us put

$$\alpha^{-1} = -ix\,2DkT \quad , \quad \langle D_N \rangle_V = (-ix)^N A_N \quad . \tag{28}$$

Therefore,

$$A_N = \alpha^N \langle |g_{jk} + \alpha^{-1}\delta_{jk}| \rangle_V \quad ; \quad g_{jj} = 0 \quad . \tag{29}$$

Note that A_N depends on x only through α.

Differentiating A_N with respect to α, and noting that the spatial averages of the minors of the diagonal elements of A_N refer to a system of N - 1 ions and that these averages are all equal, we have

$$\alpha \frac{\partial A_N}{\partial \alpha} = NA_N - NA_{N-1} \quad . \tag{30}$$

Since $\alpha \sim T^{-1}$, and since Klein's Theorem shows that A_N depends only on the variables N and $n^{1/3}/T$, let us write

$$A_N = (1 - ay^{1/3})\,[\omega(y)]^N \quad , \tag{31}$$

where

$$y = n\alpha^3 \quad , \qquad n = N/V, \qquad \lambda_m = an^{1/3},$$

with a a numerical constant. Consequently, we are to find the function $\omega(y)$ which satisfies the differential-difference equation (30) for N sufficiently large.

Using the form for A_N in Eq. (30), then

$$3y\frac{\partial\omega}{\partial y} - \frac{ay^{1/3}\omega(y)}{N(1-ay^{1/3})} = \omega - \frac{[1-a(y')^{1/3}]}{(1-ay^{1/3})}\left[\omega(y')/\omega(y)\right]^{N-1} , \tag{32}$$

where $y' = n'\alpha^3 = [(N-1)/V]\alpha^3 = y - (y/N)$.

However,

$$\omega(y') = \omega(y) - (y/N)\frac{\partial\omega}{\partial y} + \cdots \quad . \tag{33}$$

Therefore,

$$\begin{aligned}[\omega(y')/\omega(y)]^{N-1} &= \exp(N-1)\left[-(y/N\omega)\frac{\partial\omega}{\partial y} + \cdots\right] \cong \exp\left[-(y/\omega)\frac{\partial\omega}{\partial y}\right] , \\ 1 - a(y')^{1/3} &= 1 - ay^{1/3} + ay^{1/3}/3N \cdots \quad .\end{aligned} \tag{34}$$

Thus, using Eq. (34), we have in the limit N → ∞ ,

$$3y\frac{\partial\omega}{\partial y} = \omega - \exp\left[-(y/\omega)\frac{\partial\omega}{\partial y}\right] , \tag{35}$$

when $|y| < 1/a^3$.

The exact solution of Eq. (35) can be conveniently represented in parametric form. Defining

$$F(y) = -(y/\omega)\frac{\partial\omega}{\partial y} ,$$

we have

$$\omega = e^{F}/(1+3F) \quad , \quad K^2 y = F^2/(1+3F)^3 , \tag{36}$$

where K is an integration constant. Kramers has neatly determined this constant to be

$$K = \tfrac{1}{3}(4\pi)^{1/2} \tag{37}$$

by finding A_N for small concentrations. It could, of course, be found by fitting the results to the Debye-Hueckel limiting law. Eq. (36) differs from Kramers' result in that y, through α, is a function of x.

Consequently, through Eq.'s (36), (31), (28) and (24), we find that

$$\exp(g) = (-ix)e^{F}/(1+3F) . \tag{38}$$

This then yields

$$G_N = \left[1-(-ix2DkT)^{-1}\lambda_m\right]^{-1/2}\left[(1+3F)e^{-F}/(-ix)\right]^{N/2} , \tag{39}$$

where λ_m is to be found from the corresponding singularity of g.

Setting

$$z = -ix2\eta \quad , \quad \gamma^3 \equiv K^2 n(\eta/DkT)^3 , \tag{40}$$

F as a function of z is determined by

$$F^2/(1+3F)^3 = \gamma^3/z^3 \ . \tag{41}$$

Using the value of A in Eq. (10) for N large, Eq. (17) becomes

$$\exp[-\Delta\psi/kT] = (\pi N)^{1/2} e^{-N/2} I \ ,$$

$$I \equiv (2\pi i)^{-1} \int_{z_0 - i\infty}^{z_0 + i\infty} dz \left[1-(\lambda_m \eta/DkTz)\right]^{-1/2} \left[z^{-1}(1+3F)e^{-F+z}\right]^{N/2} , \tag{42}$$

where Eq. (39) has been used and the line z_o = constant, z_o real and positive, is to the right of the singularities of the integrand.

The integral I is evaluated by the method of steepest descent. The details are presented in the Appendix and we shall use the result here.

It turns out that I has two forms depending on the value of γ. For N sufficiently large, we obtain

$$-\Delta\psi/NkT = \gamma^{3/2} \qquad , \quad 0 \leqslant \gamma \leqslant \gamma_c \ , \tag{43}$$

$$-\Delta\psi/NkT = \tfrac{3}{2}(\gamma/\gamma_c) - \tfrac{1}{2}\ln(\gamma/\gamma_c) - \tfrac{5}{6} \qquad , \quad \gamma \geqslant \gamma_c \ , \tag{44}$$

with $\gamma_c = (2/3)^{2/3}$.

Discussion

We are now able, through Eq. (43) and (44), to calculate all of the thermodynamic properties of the mixture of ions. However, we will restrict ourselves to the more important quantities. It is to be recalled that $\gamma^3 = (4\pi/9)n(\eta/DkT)^3$ where η is related to the ionic strength through Eq. (6).

For the decrease $\Delta P = P - \overline{P}$ in the osmotic pressure P we have:

$$\Delta P = -\frac{\partial}{\partial v}(\Delta\psi/N) = \begin{cases} -(kT/2v)\gamma^{3/2} & , \gamma \leq \gamma_c \\ -(kT/2v)[(\gamma/\gamma_c) - \frac{1}{3}] & , \gamma \geq \gamma_c \end{cases} \tag{45}$$

where v = 1/n. Since $\overline{P}$ = (kT/v), the osmotic coefficient is given by

$$1 - g = \begin{cases} \frac{1}{2}\gamma^{3/2} & , \gamma \leq \gamma_c \\ \frac{1}{2}[(\gamma/\gamma_c) - \frac{1}{3}] & , \gamma \geq \gamma_c \end{cases} \tag{46}$$

A plot of the osmotic coefficient against the square root of the concentration is shown in Fig. 1. We obtain the Debye-Hueckel limiting law up to the equivalent concentration γ_c. Deviations from the limiting law in the proper direction set in for concentrations greater than the critical concentration.

For the decrease $\Delta\varphi$ in the thermodynamical potential we have:

$$\Delta\varphi/N = \Delta\psi/N + v\Delta P = \begin{cases} -(3/2)kT\,\gamma^{3/2} & , \gamma \leq \gamma_c \\ -kT[2(\gamma/\gamma_c) - \frac{1}{2}\ln(\gamma/\gamma_c) - 1] & , \gamma \geq \gamma_c \end{cases} \tag{47}$$

The logarithm of the activity coefficient, f_{ai}, for an ion of the ith species is defined by

$$\ln f_{ai} = (1/kT)\,\frac{\partial \Delta\psi}{\partial N_i} \tag{48}$$

We then find:

$$\ln f_{ai} = \begin{cases} -(e^2 z_i^2/\eta)(\gamma/\gamma_c)^{3/2} & ,\ \gamma \le \gamma_c \\ -\frac{1}{2}\left[(\gamma/\gamma_c) - \ln(\gamma/\gamma_c) - 1\right] - \frac{1}{2}(e^2 z_i^2/\eta)\left[3(\gamma/\gamma_c) - 1\right] & ,\ \gamma \ge \gamma_c \end{cases} \tag{49}$$

The nature of the singularity in $\Delta\psi$ at $\gamma = \gamma_c$ is easily determined to be a discontinuity in $(\partial^3 \Delta\psi/\partial\gamma^3)_{\gamma_c}$. This would mean that the osmotic coefficient is continuous with a continuous first derivative at γ_c. It is the specific heat, however, which exhibits the most unusual behavior.

We easily calculate

$$\Delta E/N = \begin{cases} -\frac{3}{2} kT\,\gamma^{3/2} & ,\ \gamma \le \gamma_c \\ -\frac{3}{2} kT\left[(\gamma/\gamma_c) - \frac{1}{3}\right] & ,\ \gamma \ge \gamma_c \end{cases} \tag{50}$$

Defining the change in specific heat by

$$\Delta C = \frac{\partial}{\partial T}(\Delta E) \quad ,$$

we find:

$$\Delta C/N = \begin{cases} (3k/4)\,\gamma^{3/2} & ,\ \gamma \le \gamma_c \\ k/2 & ,\ \gamma \ge \gamma_c \end{cases} \tag{51}$$

Consequently, the modified theory yields a constant change in specific heat above γ_c with a discontinuity in the slope at γ_c.

It is to be emphasized that although the expressions for the common thermodynamic functions change their analytical form at $\gamma = \gamma_c$, they are still continuous through the critical concentration.

The fact that the modified theory yields a limiting partition function for all concentrations of the ions as the ionic radius approaches zero, demands that a revision, and in some aspects a reversal, of Kramers' conclusions be made. The primary assumptions underlying the theory are: 1) point ions; and 2) small fluctuations. Although the same assumptions underly Kramers' theory, the assumption of small fluctuations is not adequately treated in his theory because of the use of the Gaussian charge distribution. The selection in the modified theory of those systems in Kramers' ensemble having a given ionic strength is consistent with the assumption of small fluctuations.

We believe that the existence of the discontinuity in the modified theory is due to the "association" of ions, although we are unable to demonstrate this by a pertinent calculation (except through the behavior of the osmotic coefficient, for example). It is then implied that fluctuations become significant for $\gamma > \gamma_c$. However, the association is not the catastrophe of the Kramers' theory. We may then conclude that the thermodynamic functions exist in the limit of zero ionic radius at concentrations greater than the critical concentration. A further implication is that when fluctuations become important it is also required to bring into the theory additional properties inherent in the existence of discrete charges, i.e. that $\sum_{i=1}^{s} e^4 z_i^4 = \text{constant}$.

Our interpretation of the modified theory is that for concentrations less

than the critical concentration fluctuations are unimportant and that deviations from the limiting law are indicative of the effect of finite ionic size and of the approximation of the ion-dipole (solute-solvent) interactions by a macroscopic dielectric constant. For concentrations greater than the critical, association plays an important part and this involves not only the finite ionic size and dielectric constant approximation but also the fluctuations. The modified theory does show the proper direction for the deviation of the osmotic coefficient from the Debye-Hueckel law for concentrations greater than the critical.

The critical concentration of the modified Kramers' theory is 27 times greater than the critical concentration of the Kramers' theory (Kramers' results correspond to $z \equiv 1$). For a 1-1 salt, the new critical concentration is approximately 0.81 mols/liter rather than 0.03 mols/liter. The modified theory does not, therefore, allow us to conclude that the association of point ions becomes important at small concentrations.

The result of the work of Bjerrum and Fuoss that association does become important at small concentrations is, of course, in qualitative agreement with the observations. The present theory makes it clear that one cannot avoid the introduction of the finite ionic size if even the qualitative behavior of the small concentration deviations from the Debye-Hueckel law is to be reproduced. The discontinuity at γ_c probably does not actually exist in that a finite ionic size plus fluctuations undoubtedly force association to be gradual rather than sudden, even though the suddenness is not catastrophic.

Recently, J.E. Mayer[8] developed a statistical mechanical theory of

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[8] J.E. Mayer, J. Chem. Phys. 18, 1426 (1950).

strong electrolytes which is based on the Ursell-Mayer cluster integral expansion. His approach is probably more suitable than ours if one wishes to take the detailed ion-dipole interaction and van der Waals forces between ions into account. Since it is practically impossible to evaluate all the required cluster integrals, Mayer limits his main calculation to finding the contribution of the so-called ring clusters (in which each particle interacts with only two others) to various thermodynamic quantities. This contribution seems to be the part of the complete expansion which gives rise to the Debye-Hueckel approximation. Since we obtained similar results, it appears that sphericalization (the condition expressed by Eq. (7)) and the neglect of all cluster integrals except rings give almost equivalent approximations to the partition function.

It has been emphasized by Mayer that the long range coulomb forces lead to difficulties in the evaluation of the partition function of a system of ions. The difficulties are avoided in his theory by the replacement of the coulomb law with $(\epsilon_i \epsilon_j /r) \exp(-\mu r)$ where μ is a very small positive number. At short distances this expression reduces to the coulomb law, but at large distances where electrical neutrality prevents a physical divergence in thermodynamic quantities, the factor $\exp(-\mu r)$ prevents a mathematical divergence in the partition function. Mayer's final results become independent of μ as $\mu \rightarrow 0$. The present analysis has also shown the utility of the convergence or summability factor $\exp(-\mu r)$. It was useful not only to prevent a possible divergence but to insure the existence of a limiting free energy per particle which is necessary for the application of Klein's Theorem. As in the Mayer theory, if one takes into account the electrical neutrality at every step in the analysis it should not be necessary to introduce the

convergence factor. However, since this requires a much more extensive analysis we have avoided it.

The above analysis had its origin in the work of M. Kac on the Gaussian model of a ferromagnet and of M. Kac and the authors on the spherical model of cooperative phenomena.[9]

The authors wish to thank Mr. L. Witten for several discussions and his aid in preparing the Figures.

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[9] Kac, M. and Berlin, T.H., Phys. Rev. 75 1298 (1949). Montroll, E Nuovo Cimento Supplemento VI, 266 (1949).

APPENDIX

We shall present here the details of the evaluation by the method of steepest descent of the integral in Eq. (42).

$$I = (2\pi i)^{-1} \int_{z_0 - i\infty}^{z_0 + i\infty} dz \left[1 - (\lambda_m \eta / DkTz\right]^{-1/2} \left[z^{-1}(1+3F)\exp(-F+z)\right]^{N/2}, \tag{A 1}$$

where $F^2/(1+3F)^3 = \gamma^3/z^3$,

and the line z_o = constant, z_o real and positive, is to the right of the singularities of the integrand.

The function F is a three-valued function of z. We can construct a Riemann surface of three sheets to make F an analytic function of z.

Let $\varrho = (z/3\gamma)^3$. The solutions of the cubic equation for F,

are:

$$\begin{aligned} F_1(z) &= \tfrac{1}{3}(\varrho - 1) - \omega^2 L^{1/3} - \omega M^{1/3} ; \\ F_2(z) &= \tfrac{1}{3}(\varrho - 1) - \omega L^{1/3} - \omega^2 M^{1/3} ; \\ F_3(z) &= \tfrac{1}{3}(\varrho - 1) - L^{1/3} - M^{1/3} ; \end{aligned} \tag{A 2}$$

the subscripts denoting the different sheets of the Riemann surface, and where

$$\begin{aligned} \omega &= \exp(i2\pi/3), \\ L &= -(\varrho/27)(\varrho^2 - 2\varrho + \tfrac{3}{2}) + i(\varrho/27)(\varrho - \tfrac{9}{4})^{1/2}, \\ M &= -(\varrho/27)(\varrho^2 - 2\varrho + \tfrac{3}{2}) - i(\varrho/27)(\varrho - \tfrac{9}{4})^{1/2}. \end{aligned} \tag{A 3}$$

The discriminant of the cubic is $(4\varrho^2/27)(\varrho - \frac{9}{4})$.

The branch points occur when the discriminant equals zero and are $\varrho = 0, \frac{9}{4}$,

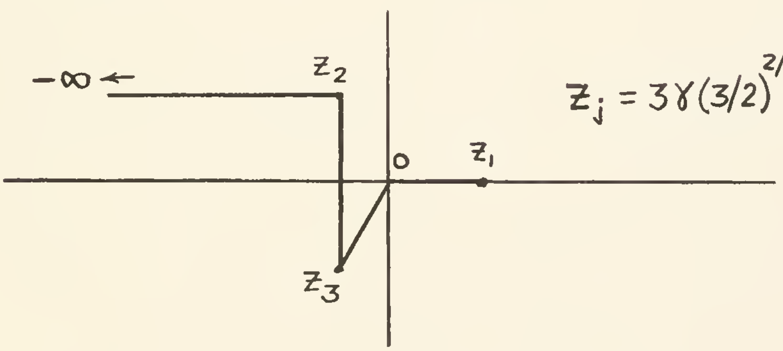
and this means that the cubic has multiple roots. Note that the point at infinity is a branch point since $L \rightarrow M$ as $|\xi| \rightarrow \infty$. The values of z at the branch points are $z = 0$, $3\gamma(3/2)^{2/3}$, $3\gamma(3/2)^{2/3}\omega$, and $3\gamma(3/2)^{2/3}\omega^2$. Consequently, in the expression (A 1) for I, we must take $z_o > 3\gamma(3/2)^{2/3}$. Furthermore, λ_m corresponds to this largest, real, and positive singularity, and we conclude that

$$1 - (\lambda_m \eta / DkTz) = 1 - 3\gamma(3/2)^{2/3} z^{-1}, \tag{A 4}$$

or

$$\lambda_m = 3\pi^{1/3} n^{1/3}.$$

By constructing a cut in the z-plane as shown in Fig. A 1, F_j is analytic in the cut plane.



$$z_j = 3\gamma(3/2)^{2/3} \exp[i(2\pi/3)(j-1)]$$

Fig. A 1. The branch cuts in the complex z-plane

Let us write

$$e^G = z^{-1}(1 + 3F)e^{-F+z}$$

or (A 5)

$$G = z - \ln z - F + \ln(3F + 1),$$

and attempt to find a saddle point. We have

$$dG/dz = z^{-1}(z - 1 - 3F) \tag{A 6}$$

and

$$d^2G/dz^2 = 2(1 + 3F)^2/z^2(2 - 3F). \tag{A 7}$$

Letting z_s be such that $(dG/dz)_{z_s} = 0$, then

$$z_s = 1 + 3F(z_s). \tag{A 8}$$

Using the relation between F and z, we obtain

$$F(z_s) = \pm \gamma^{3/2}, \quad z_s = 1 \pm 3\gamma^{3/2} \tag{A 9}$$

Also

$$(d^2G/dz^2)_{z_s} = 2/(3 - z_s). \tag{A 10}$$

We conclude that a saddle point exists for γ in the range $0 \leqslant \gamma < \infty$ when $z_s = z_- = 1 - 3\gamma^{3/2}$, and that a saddle point exists for $z_s = z_+ = 1 + 3\gamma^{3/2}$ for γ in the range $0 \leqslant \gamma < \gamma_c = (2/3)^{2/3}$. When $\gamma = \gamma_c$, $z_+ = 3$, and the second derivative of G becomes infinite. For $\gamma \simeq 0$, $z_s \simeq 1$, and since $\xi = (z/3\gamma)^3$, $|\xi| \simeq (3\gamma)^{-3} \sim \infty$. It is easily found that when $|\xi| \to \infty$,

$$\begin{aligned} F_1(z) &= +\tfrac{1}{9}(3/\xi)^{1/2} + (6\xi)^{-1} \cdots, \\ F_2(z) &= -\tfrac{1}{9}(3/\xi)^{1/2} + (6\xi)^{-1} - \cdots, \\ F_3(z) &= \xi - 1 - (3\xi)^{-1} - \cdots. \end{aligned} \tag{A 11}$$

Therefore, the branch $F_1(z)$ corresponds to $F(z_+) = +\gamma^{3/2}$ and the branch $F_2(z)$ corresponds to $F(z_-) = -\gamma^{3/2}$.

From Eq. (A 5),

$$G(z_s) = z_s - F(z_s) = 1 + 2F(z_s),$$

so that

$$G(z_+) = 1 + 2\gamma^{3/2} \quad \text{and} \quad G(z_-) = 1 - 2\gamma^{3/2}. \qquad \text{(A 12)}$$

Since for large N, I is essentially $\exp\left[NG(z_+)/2\right]$ or $\exp\left[NG(z_-)/2\right]$, it is plain from Eq. (42) of the text, where

$$\exp\left[-\Delta\psi/kT\right] = (\pi N)^{1/2} e^{-N/2} I ,$$

that the significant contribution to I arises from the saddle point z_+. As a consequence the integral I is to be evaluated on sheet 1 where we require $F(z) \equiv F_1(z)$. This means that we can now write

$$I \simeq (2\pi i)^{-1} \int_{z_+ - i\infty}^{z_+ + i\infty} dz \left[1 - 3\gamma(3/2)^{2/3} z^{-1}\right]^{-1/2} \exp \frac{N}{2}\left[G(z_+) + \frac{1}{2}(d^2G/dz^2)_{z_+}(z - z_+)^2 \cdots\right]$$

so that

$$I \simeq \left[1 - 3\gamma(3/2)^{2/3} z_+^{-1}\right]^{-1/2} \left[\pi N (d^2G/dz^2)_{z_+}\right]^{-1/2} \exp\left[NG(z_+)/2\right]. \qquad \text{(A 13)}$$

Hence,

$$\exp\left[-\Delta\psi/kT\right] = \left[1 - (3\gamma/z_+\gamma_c)\right]^{-1/2} \left[1 - (\gamma/\gamma_c)^{3/2}\right]^{-1/2} \exp\left[N\gamma^{3/2}\right], \qquad \text{(A 14)}$$

and for N very large,

$$-\Delta\psi/NkT = \gamma^{3/2}, \qquad \gamma < \gamma_c = (2/3)^{2/3}. \qquad \text{(A 15)}$$

As $\gamma \rightarrow \gamma_c$, the saddle point $z_+ \rightarrow 3$, a branch point of F, and the derivative $\left[d^2G/dz^2\right]_{z_+} \rightarrow \infty$. It would appear that the branch point limits

the validity of the integral I because if we use the above saddle point equations for $\gamma > \gamma_c$, then $z_+ > 3$, the second derivative of G changes sign and the path of steepest descent is along the real axis. This would make I, and $\Delta\psi$ purely imaginary as can be seen by analytically continuing Eq. (A 14). The apparent limitation is equivalent to the breakdown found by Kramers. His formulas become meaningless when $\gamma = \gamma_c$ and the branch point is reached, because his equations become undefined for $\gamma > \gamma_c$.

The path along the real axis through the saddle point z_+ is not mathematically legitimate for $\gamma > \gamma_c$ because the imaginary part of G(z) for this path is identically zero. This path of steepest descent can not be deformed into the original path, the line for which the real part of z equals z_o. We therefore suppose that $\gamma > \gamma_c$ and investigate in further detail the behavior of the integrand in the neighborhood of the branch point of F, $\xi = 9/4$.

Let us set $\xi = (9/4) + \epsilon$ with $|\epsilon|$ very small. Then, since $z = 3\gamma\xi^{1/3}$,

$$z = 3(\gamma/\gamma_c)\left[1 + (4/27)\epsilon - \cdots\right].$$

Furthermore,

$$F_1(z) = (2/3) - (4\cdot 3^{1/2}/9)\epsilon^{1/2} + (40/81)\epsilon - (592\cdot 3^{1/2}/243)\epsilon^{3/2}\cdots. \qquad \text{(A 16)}$$

From the definition of G(z), we then obtain

$$G(z) = G_o + G_o'\epsilon + \alpha\epsilon^{3/2} \cdots, \qquad \text{(A 17)}$$

where

$$G_o = 3(\gamma/\gamma_c) - \ln(\gamma/\gamma_c) - 2/3,$$

$$G_o' = (4/9)\left[(\gamma/\gamma_c) - 1\right], \qquad \text{(A 18)}$$

$$\alpha = 32\cdot 3^{1/2}/243.$$

Now when $\gamma > \gamma_c$, we note that $G'_o > 0$. Consequently, for $|\epsilon|$ small and real part of ϵ negative, G(z) has a maximum value, G_o, at $\epsilon = 0$, $z = z_1 = 3(\gamma/\gamma_c)$. The remaining question concerns the possibility of locating a path of steepest descent, imaginary part of G(z) = 0, which can be deformed into the original path. If we set $\epsilon = re^{i\theta}$ with r small,

$$\text{imaginary part of } G(z) = G'_o r \operatorname{Sin}\theta + \alpha r^{3/2} \operatorname{Sin}(3\theta/2). \qquad \text{(A 19)}$$

Setting this equal to zero, we have for the possible path

$$r^{1/2} = -(G'_o/\alpha)\,\frac{\operatorname{Sin}\theta}{\operatorname{Sin}(3\theta/2)} \qquad \text{(A 20)}$$

The path cannot cross the cut from 0 to $z_1 = 3(\gamma/\gamma_c)$ in Fig. A 1. Therefore, in the upper half plane we take $\theta = \pi - \varphi$ and in the lower half plane we take $\theta = -\pi + \varphi$ where φ is positive and small in both cases. Hence

$$r^{1/2} = -(G'_o/\alpha)\,\frac{\operatorname{Sin}\varphi}{-\operatorname{Cos}(3\varphi/2)} \cong (G'_o/\alpha)\varphi\,, \qquad \text{(A 21)}$$

and a path not on the real axis exists on both sides of the cut. The path is shown in Fig. A 2.

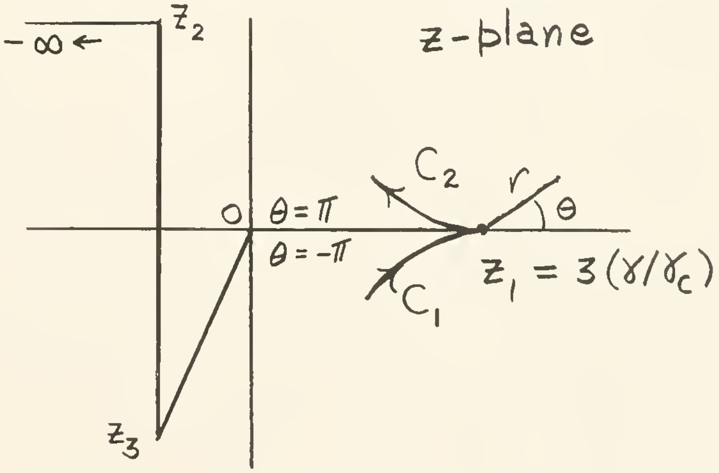


Fig. A 2. Path of steepest descent for $\gamma > \gamma_c$.

In the neighborhood of z_1, the integrand becomes infinite like

$$[1-(3\gamma/z\gamma_c)]^{-1/2} \simeq (27/4\epsilon)^{1/2} ,$$

and, as a consequence, the contribution to I from an infinitesimally small path circling z_1 is zero in the limit. The integral may then be written

$$I \simeq (2\pi i)^{-1} \int_{C_1+C_2} (4\gamma/9\gamma_c)\, d\epsilon\, (27/4\epsilon)^{1/2} \exp\left[(N/2)(G_0 + G_0'\epsilon - -)\right] . \qquad \text{(A 22)}$$

For N very large the maximum is very sharp and the contributions to I arise from the parts of C_1 and C_2 very near the branch point. Therefore, the contributing parts of C_1 and C_2 may be replaced by integrals along the real axis. In C_1 we may use $\epsilon = re^{-i\pi}$, $\infty > r \geq 0$, and in C_2 we may use $\epsilon = re^{i\pi}$, $0 \leq r < \infty$. Hence,

$$I \simeq (2\pi i)^{-1}(4\gamma/9\gamma_c)(27/4)^{1/2} \int_{\infty}^{0} (-dr)\, r^{-1/2} e^{i\pi/2} \exp\left[(N/2)(G_0 - G_0' r)\right] \qquad \text{(A 23)}$$

$$+ (2\pi i)^{-1}(4\gamma/9\gamma_c)(27/4)^{1/2} \int_{0}^{\infty} (-dr)\, r^{-1/2} e^{-i\pi/2} \exp\left[(N/2)(G_0 - G_0' r)\right] ,$$

and

$$I \simeq 2(2/3)^{1/2}(\gamma/\gamma_c)(\pi N G_0')^{-1/2} \exp\left[N G_0/2\right] . \qquad \text{(A 24)}$$

Finally,

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$$\exp[-\Delta\psi/kT] \simeq 2(3/2)^{1/2}(\gamma/\gamma_c)[(\gamma/\gamma_c)-1]^{-1/2}\exp[(N/2)(G_o-1)], \qquad \text{(A 25)}$$

and for N very large,

$$-\Delta\psi/NkT = \frac{3}{2}(\gamma/\gamma_c) - \frac{1}{2}\ln(\gamma/\gamma_c) - \frac{5}{6} \quad , \quad \gamma > \gamma_c = (2/3)^{2/3}. \qquad \text{(A 26)}$$

We note from Eq. (A 15) and (A 26) that $\Delta\psi$ is continuous when $\gamma = \gamma_c$:

$$-\Delta\psi/NkT = 2/3 \quad , \quad \gamma = \gamma_c . \qquad \text{(A 27)}$$